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ADP023617

TITLE: Thermodynamic, Transport and Chemical Properties of "Reference" JP-8

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THERMODYNAMIC, TRANSPORT AND CHEMICAL PROPERTIES OF "REFERENCE" JP-8

(Contract Number F1ATA06004G004)

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SUMMARY/OVERVIEW:

The NIST research focuses on measurement of major thermophysical and chemical properties of JP-8, to develop it as a reference fluid. The properties include fluid volatility, density, speed of sound, viscosity and thermal conductivity. In addition, we are assessing the global thermal decomposition of the fluid, primarily to guide our property measurements. The measured properties will be used to develop a predictive surrogate fluid model for real JP-8. Three different samples of JP-8 have been obtained, and measurements are in progress on all three.

TECHNICAL DISCUSSION

Chemical Analysis:

A chemical analysis was done on each of the fluid samples by gas chromatography mass spectrometry ((30 m capillary column of 5% phenyl polydimethyl siloxane having a thickness of 1 μm, temperature program from 90 to 250 °C, 10 °C per minute). Mass spectra were collected for each peak from 15 to 550 RMM (relative molecular mass) units. Chromatographic peaks made up of individual mass spectra were examined for peak purity, then the mass spectra were used for qualitative identification. Components in excess of 0.5 mole percent were selected for identification and tabulated for each fluid. In addition to this detailed analysis, the hydrocarbon type classification based on ASTM D-2789 was performed. These results figure in the overall mixture characterization, and are also used for comparisons with the chemical analyses of individual distillate fractions (discussed in the section on distillation curves).

Thermal Decomposition:

The thermal decomposition of the JP-8 fluids is being assessed with an ampoule testing instrument and approach that has been developed at NIST[1-4]. It must be understood that this work is meant strictly to support the physical property measurement work, and not to delineate reaction mechanisms. The instrument we developed consists of a 304L stainless steel thermal block that is heated to the desired experimental temperature (here, from 250 – 425 °C). The block is supported in an insulated box with carbon rods; the temperature is maintained and controlled (by a PID controller) to within 0.1 °C in response to a platinum resistance sensor embedded in the thermal block. The ampoule cells consist of 6.4 cm lengths of ultrahigh pressure 316L stainless steel tubing (0.64 cm external diameter, 0.18 cm internal diameter) that are sealed on one end with a stainless steel plug welded by a clean tungsten-inert-gas (TIG)

process. Each cell is connected to a high-pressure high-temperature valve at the other end with a short length of 0.16 cm diameter 316 stainless steel tubing with an internal diameter of 0.02 cm, also TIG welded to the cell. Each cell and valve is capable of withstanding a pressure in excess of 105 MPa at the desired temperature. The internal volume of each cell is known and remains constant at a given temperature. Fluid is added to the individual cell by mass (as determined by an approximate equation of state calculation) to give a total pressure of 34 MPa at the final fluid temperature. Thus far, we have completed measurements at 250, 275, 300, and 350 °C. From 250 – 300 °C, little if any decomposition was noted. Decomposition began at 350 °C, and work at 375 °C is in progress.

Distillation Curves:

In previous work, several significant improvements in the measurement of distillation curves for complex fluids were introduced. The modifications to the classical measurement provide for (1) temperature and volume measurements of low uncertainty, (2) temperature control based upon fluid behavior, and most important, (3) a composition-explicit data channel in addition to the usual temperature-volume relationship[5-8]. This latter modification is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. Moreover, as part of the improved approach, the distillation temperature is measured in two locations. The temperature is measured in the usual location, at the bottom of the take-off in the distillation head, but it is also measured directly in the fluid. The measurement in the fluid is a valid thermodynamic state point that can be theoretically explained and modeled. The usual temperature measurement location (in the head) provides a temperature that is not a thermodynamic state point, but which is comparable to historical measurements made for many decades. We also use a modification of the Sidney Young equation (to correct the temperatures to standard atmospheric pressure) in which explicit account is taken of the average length of the carbon chains of the fluid. As applied to JP-8, we have measured the distillation curve of three separate lots of fluid with the new approach. The curves, examples of which are provided in Figure 1, show clearly the variability in the fluids; two are similar in volatility while the third is very different. For each fluid, we have collected sample aliquots of each distillate volume fraction for analysis by GC-MS. These individual fractions have been analyzed, and energy content calculations are planned. In addition, for each fraction, the ASTM D-2789 analysis has been done.

Thermophysical Properties:

The density, viscosity, and speed of sound of three JP-8 samples are being measured in two commercial rapid characterization instruments. A Stabinger viscodensimeter was used to determine the density and the absolute and kinematic viscosity in the temperature range from −40 °C to 100 °C (233.15 K to 373.15 K) at atmospheric pressure. A sound-speed analyzer was used to measure the speed of sound and the density of the JP-10 samples at atmospheric pressure in the temperature range from 5 °C to 70 °C (278.15 K to 343.15 K). The measurements with the Stabinger viscodensimeter were carried out according to ASTM Standard D 7042 – 04 *Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity).* Combining a densimeter with a speed of sound measurement makes it possible to obtain the adiabatic compressibility $\kappa_s = -(\partial V/\partial p)_s/V = 1 / (\rho w^2)$ where V denotes volume, p is pressure, and w the speed of sound. The viscometer part of the instrument uses a rotational coaxial cylinder measuring system. The rotational speed of the inner cylinder establishes itself as the result of the equilibrium between the driving torque of the viscous forces and the retarding eddy current torque. This rotational speed is measured by an electronic system (Hall effect sensor) that counts the frequency of the rotating magnetic field of a

magnet and a soft iron ring. The digital density analyzer in the viscodensimeter uses a U-shaped vibrating sample tube and a system for electronic excitation and frequency counting. The density of the sample liquid in the vibrating tube is obtained from the resonant frequency of the vibrating system relative to the resonant frequency with a calibration liquid of known density.
The combination of a viscometer and a densimeter makes it possible to obtain absolute viscosity η as well as kinematic viscosity ν of a sample. This apparatus is depicted in Figure 2. We anticipate measurements of all fluids (at atmospheric pressure) between -40 and 100 °C.

In addition to these atmospheric pressure instruments, an apparatus has been designed and built for the rapid screening of liquid densities over the temperature range of 0 to 200 °C and pressures to 45 MPa. The heart of the apparatus is a commercial vibrating tube densimeter, modified at NIST. The densimeter is housed in a specially designed two-stage thermostat for precise temperature control. The uncertainty in the temperature is 0.03 °C with short-term stability of 0.005 °C. Pressures are measured with an oscillating quartz crystal pressure transducer with an uncertainty of 5 kPa. The densimeter is calibrated with measurements of vacuum, propane and toluene, over the temperature and pressure range of the apparatus to achieve an uncertainty in density of 1 kg/m^3. Thus far, one sample lot of JP-8 has been measured from 0-200 °C, and from 1 – 30 MPa. Work on the second and third fluid samples is ongoing.

Model Development:
Upon completion of the experimental measurements of the physical and chemical properties described above, a model for the fluid will be developed. This model will be explicit in Helmholtz energy as a function of density and temperature. All single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy. A preliminary equation of state for propane will be used as the starting point for the equation of state. The properties of individual mixture components, identified and evaluated in the experimental steps above, will be incorporated into the mixture model.

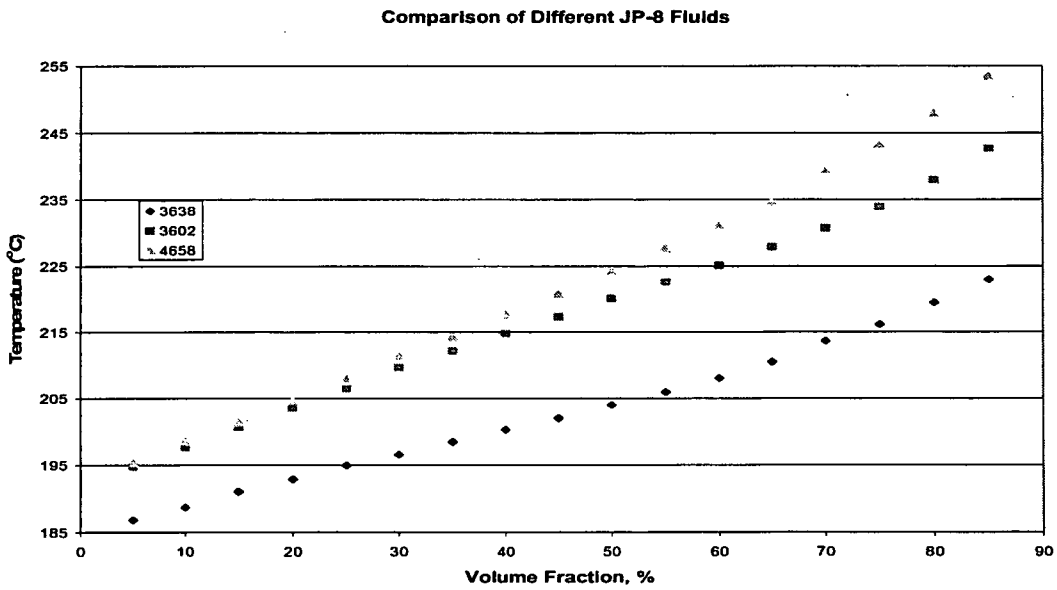

Figure 1: The distillation curves of three different lots of JP-8, showing the variability that can be encountered.

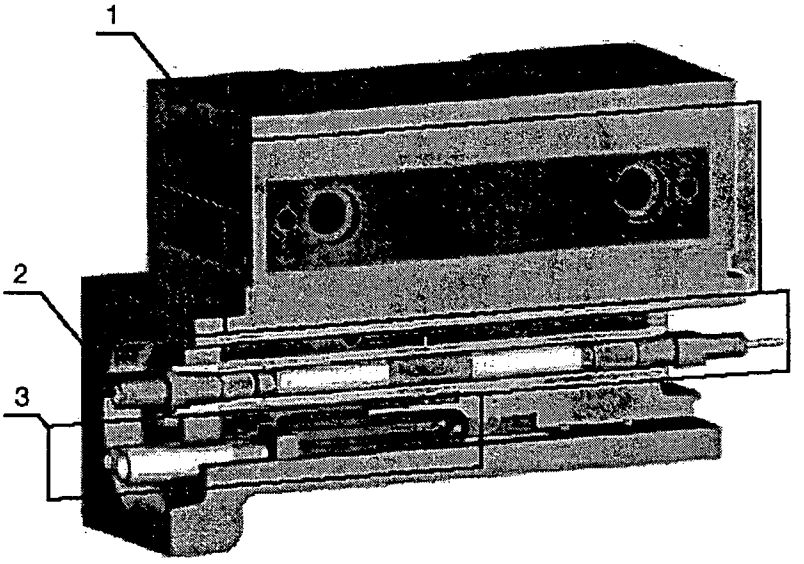

Figure 2: Main components of the Stabinger viscodensimeter SVM 3000.
1 – Thermostatting Peltier block, 2 – Concentric cylinder viscometer, 3 – Vibrating tube densimeter.

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